THERMAL DIFFUSION NEAR THE CRITICAL POINT

BY

EDWARD BONFOY GILLER

B.S., University of Illinois, 1940
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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Introduction

Thermal diffusion is the transport of molecules of a mixture caused by a temperature gradient. The steady state concentration gradient of the mixture is such that the rate of separation caused by thermal diffusion is balanced by the remixing effect of ordinary diffusion.

The thermal diffusion coefficient is peculiar among the gas coefficients (diffusion, viscosity, thermal conductivity) in that its value is extremely sensitive to the interaction potential existing between the molecules. The law of molecular interaction may be determined by thermal diffusion measurements. Because of this sensitivity to the molecular model, thermal diffusion measurements afford a most powerful method for investigating the molecular behavior in the transition region between dense gas and liquid phases.

The separation caused by thermal diffusion in the critical region of the gas mixture xenon-ethane was measured experimentally. α, which is related to the thermal diffusion and ordinary diffusion coefficients by Equation 1, was calculated from column theory. α, the thermal diffusion ratio, was then used to study the molecular interaction occurring in the critical region.

$$\alpha = \frac{D_T}{n_{10}\, n_{20}\, D_{12}} \tag{1}$$

Thermal diffusion measurements were made on the system xenon-ethane at pressure from 4.23 to 99.63 atm. and temperatures from -15.10 to $54.60°$ C. with special emphasis placed on the critical region. The experiments covered a density range of from 0.0050 to 0.339 grams per cubic centimeter. The system xenon-ethane was chosen for its advantage of a narrow critical envelope, knowledge of its physical properties, molecular symmetry, and ease of accurate control and analysis.

The dilute concentration of xenon was analyzed continuously by a radioactive Xe^{133} tracer using a novel and original application of light transmission from scintillation crystals within the column to external photomultiplier tube counters.

Theory

Chapman and Cowling (1) have presented a very comprehensive derivation of the gas coefficients. They present the thermal diffusion ratio in terms of certain $\Omega^{(l)}_{(r)}$ integrals which are functions of the molecular model. Hirshfelder et al. (4) have evaluated the integrals in terms of certain $W^{(l)}_{(r)}$ integrals for the Lennard-Jones model, a relatively realistic law of molecular interaction which predicts very accurately the viscosity and thermal conductivity for dense gases. The values of α are calculated from the column theory of Furry and his co-workers (2,3) and then corrected for column hydrodynamics by the dimensionless group correlation of Tung and Drickamer (6). By applying Thorne's (5) dense gas correction to the derivation of Chapman and Cowling for the thermal diffusion ratio where one component is in infinite dilution, and making certain assumptions, it was possible to calculate the cluster sizes necessary to explain the experimental results obtained.

Experimental Apparatus

The investigation was conducted in two separate columns each 40.3 cm. in length. The annular spacing used was 0.02″ and 0.04″. Pressures were measured by a dead weight type gage and temperatures were measured with thermocouples. A new and very useful device is described in detail for the internal continuous analysis within a closed high pressure system. This device concerns the use of anthracene phosphor crystals which will give the radioactive tracer concentration by transmitting the radioactive disintegration light pulses in the crystal through a lucite rod to a photomultiplier type of vacuum tube and thence to a counting circuit. A high pressure fitting utilizing 'O-Rings' was developed for the lucite rod.

Results and Conclusions

The values of a are tabulated and shown graphically as a function of temperature and density. The physical properties of the gas system xenon-ethane are presented and the following conclusions drawn.

1. There is no discontinuity between liquid and dense gas as far as the thermal diffusion ratio is concerned.

2. The assumption of molecular chaos is not applicable to xenon-ethane gas mixture in the critical region due to the formation of 'clusters' of ethane and xenon.

3. The ethane molecules will form clusters of a maximum average of 50 molecules per cluster in the critical region close to the phase envelope. These clusters will decrease in size, at constant density, with increasing temperature.

4. The xenon molecules will form clusters above a density of 0.16 gm./cc. reaching a maximum of 16 molecules per cluster near the phase envelope. The xenon cluster will decrease in size, at constant density, with increasing temperature.

5. Ethane will form clusters at densities as low as 0.01 gm./cc. These clusters will average 2-3 molecules per cluster and show little change in size, at constant density, with increasing temperature.

6. The value of a predicted by the dense gas correction to the Lennard-Jones model is not of the correct sign or order of magnitude except at very low densities where it is of the correct sign only.

7. Even with definite turbulent heat transfer occurring within the column, separation occurs in the laminar layer which is of the same order of magnitude as the separation obtained when the column is operated below the turbulent level.

8. A very useful high pressure device is described where-

by using radioactive tracers it is possible to analyze continuously within a closed system.

Nomenclature

D_T	thermal diffusion coefficient
D_{12}	diffusion coefficient
n_{i0}	mole fraction of component i
α	the thermal diffusion ratio

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VITA

The author was born in White Hall, Illinois on July 8, 1918. He graduated from High School at Kemper Military School in 1936. After one year of Junior College at Kemper, he transferred to the University of Illinois and graduated with a Bachelor of Science in Chemical Engineering in 1940. Following one year of employment as a Junior Chemical Engineer with Sinclair Refining Company at Houston, Texas, he joined the United States Air Force. During the three years overseas duty between 1943 and 1946, the author was awarded the Silver Star and advanced to the rank of Lieutenant Colonel. Upon return to the United States in 1946, he entered the University of Illinois Graduate School under auspices of the United States Air Force. He was awarded the Degree of Master of Science in Chemical Engineering in 1948. The author is a member of Sigma Xi.

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